STUDIES ON OPTICAL AND ELECTRICAL PROPERTIES OF PURE AND DOPED TRIGLYCINE SULPHATE CRYSTALS

SYNOPSIS OF THE THESIS

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SYNOPSIS

Ferroelectric Triglycine sulphate crystal (TGS) is a potential material for the infrared detection by virtue of its high pyroelectric coefficient (λ) and low dielectric constant (ε'). This crystal has a typical second order phase transition (ferroelectric ↔ paraelectric) at the Curie temperature 49°C. The X-ray analysis has shown that the crystal symmetry of TGS is monoclinic with the space group $P2_1$ in the ferroelectric phase and in the paraelectric phase the structure exhibits two mirror planes at y = ¼ and y = ¾ and the space group becomes $P2_1/m$. Below the Curie temperature TGS exists in a typical uniaxial ferroelectric phase. The spontaneous polarisation is along the b-axis. However TGS crystal has a disadvantage of depolarization as time elapses. Research and Development efforts have been mainly concentrated towards further improvement in the pyroelectric properties of TGS with wide variety of dopants because of its potential application in infrared (IR) detectors.

Ferroelectric TGS crystals are an interesting class of materials. They are phenomenological to ferromagnetic materials in that they exhibit hysteresis loops, spontaneous polarization and coercive field. These crystals have a number of practical applications and one of those is a pyroelectric infrared (PIR) detection. The heart of every PIR detector is the pyroelectric sensor. PIR devices can detect a person moving into or through a detection zone with high reliability. The slightest positive or negative thermal radiation change in contrast to a background, focused by the appropriate optics, triggers the sensor element. There is no interference between neighboring units due to the passive nature of the detection principle. The use of differential or dual-channel sensor technology and advanced digital signal processing reduces false alarms caused by

turbulence. Similarly, precision optics accurately defines the field of view, allowing consistent and long-range coverage.

Typical sensors use pyroelectric materials, such as tri-glycine sulphate (TGS) or lithium tantalite, which undergo a change in polarization if the temperature of the material is altered (in the case of PIR detectors by thermal radiation). If electrodes are placed on opposite faces of a thin slice of the material to form a capacitor, the change in polarization can be observed as an induced voltage across the slice if the external impedance is comparatively high. The sensor produces an electrical output signal when the temperature of the incident radiation changes. A differential sensor uses two elements of opposite polarity so that equal radiation changes on both elements are compensated to zero output. Both TGS and lithium tantalite exhibit a large spontaneous electrical polarization below T_c, known as the Curie point.

A systematic survey of the literature in this field shows that efforts made to tailor the properties of TGS crystals for practical device design requirements led to numerous studies on TGS doped with organic and/or inorganic dopants including various metal ions. However, a few of the dopants used to dope TGS have failed to meet the standards set by device applications. Hence, there is a need to search for new dopants which can provide good optical quality crystals rich with desired ferroelectric properties. In this context, the present thesis is focused on the growth and characterization of pure and new organic molecule doped TGS single crystals. Also the electron radiation effects on the optical and electrical properties are discussed in detail. Crystals of TGS doped with new organic dopants are able to reduce the depolarization effect, increase in pyroelectric coefficient, reduction in dielectric constant, improvement in figures of merit, increase in transition temperature and improvement in hardness number. Crystals grown are of good optical quality. The new dopants used are 4-(dimethylamino) benzaldehyde

[$(CH_3)_2$ NC_6H_4CHO], Iminodiacetic acid [$HN(CH_2COOH)_2$], n-bromo succinimide [$C_4H_4BrNO_2$] and Succinic acid [$(CH_2COOH)_2$].

The major problem faced with the TGS crystal is the depolarization as time elapses. The best known methods of stabilizing spontaneous polarization in water soluble ferroelectric crystals are the introduction of impurities into the crystals and irradiation of already grown crystals. In both the cases the appearance of unipolarity is associated with the formation of internal fields in crystals. It has been shown both theoretically and experimentally that internal bias fields in impurity containing crystals can be explained by the existence of the electric and mechanical stresses caused by the formation of a nonsymmetrical impurity distribution during crystal growth. Therefore, it is important to develop methods for control of unipolarity and establish the factors governing this effect. Large number of dopants was tried by various researchers to improve the property of the TGS crystals but very few radiation damage studies are reported. The effect of electron radiation on the optical, dielectric and ferroelectric properties is of considerable interest as it significantly modifies the physical properties of these materials.

The crystals used for the studies were grown using solution growth method at ambient temperature and few at constant temperature. Number of optical quality crystals of different size was grown in each dopant concentration for the investigation.

The thesis consists of eight chapters. The First chapter deals with a review of ferroelectric materials. The classification of ferroelectric materials and various physical properties of ferroelectric crystals are discussed in brief. The motivation and scope of the present research work are also presented in this chapter.

The Second chapter describes the various techniques employed for the growth of bulk single crystals. The principles of crystal growth, growth kinetics, factors affecting growth etc of TGS are also discussed in this chapter. This chapter also gives an account

of the experimental techniques used to grow and characterize pure and doped TGS crystals. The experiments are performed on 010 plates cut perpendicular to the ferroelectric b-axis of these crystals grown in the laboratory using the solution growth setup. Preliminary characterization techniques like powder X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy, Vickers hardness test are described briefly. Principles of the characterization techniques are also presented in this chapter. Experimental methods and the instrumentation used for the dielectric, pyroelectric, piezoelectric, hysteresis, and DC conductivity measurement of the grown crystals are explained. An account of electron irradiation technique is also given in this chapter.

The Third chapter deals with the synthesis and growth of TGS single crystals doped with 4-(dimethylamino) benzaldehyde [$(CH_3)_2NC_6H_4CHO$], Iminodiacetic acid [$HN(CH_2COOH)_2$], n-bromosuccinimide [$C_4H_4BrNO_2$] and Succinic acid [$(CH_2COOH)_2$] by slow evaporation method. The characterization of the synthesized material for their identity by various solid-state characterization methods like X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Morphology, Hardness and piezoelectric property are discussed. The X-ray diffraction data of all the samples were collected and the data was analysed to determine the structural parameters of the crystals. The FT-IR spectra in the mid IR (4000 -500cm^{-1}) have been analysed in detail. The Morphology of the grown crystals is studied. The Vickers hardness characteristics of the grown crystals are discussed in detail. The piezoelectric coefficients of the crystals are determined at room temperature.

In the Fourth chapter, studies performed on the optical properties of the crystals using UV-visible spectrum are discussed. The UV-Visible spectra were recorded in the wavelength range of 195 – 1000nm for unirradiated and the crystals irradiated with 8MeV

electron energy. The optical cut-off wavelength and optical band gap of the materials are calculated. The effects of electron irradiation on the optical property of these crystals are presented and discussed.

Chapter Five deals with the studies on dielectric property of the grown crystals as a function of temperature. The variation of inverse dielectric constant as a function of temperature is also investigated to evaluate Curie constants both in the paraelectric and ferroelectric phases and transition temperature is estimated. The effects of 8MeV electron radiation of different doses from 5kGy to 80 kGy on the dielectric properties of these crystals are also investigated.

The Sixth chapter deals with the pyroelectric properties of pure and doped TGS crystals with different doping concentrations. The one of the parameter found very important in selecting the crystal to use in pyroelectric detector applications is Figure of merit. The Figure of merit for high current responsivity, Figure of merit for high voltage responsivity, Figure of merit for vidicon application are calculated for all the crystals and presented in this chapter. Variation of Figure of merit as a function of temperature is also investigated. In the present investigation the effect of 8MeV electron radiation on the pyroelectric properties of these crystals are also investigated. The modifications in the Figure of merit due to irradiation are also discussed in detail.

Seventh chapter describes the investigations performed on the internal bias field and its effects on the electrical properties. In some of the samples large internal bias field is observed. This reduces the depolarization effect in the TGS crystal significantly. The temperature dependence of DC conductivity is also discussed in this chapter. The activation energies both in ferroelectric and paraelectric phases have been estimated.

Eighth chapter gives the overall summary of the present investigation. Comprehensive comparisons of different properties of pure and doped TGS crystals are

discussed. The scope for further study in this area has been assessed. Each chapter ends with conclusions and references.

The results of the present investigations have been published in refereed journals and some are presented in the national and international conferences/symposiums.

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List of publications resulting from this thesis

1. Growth of 4-(dimethylamino) benzaldehyde doped Triglycine Sulphate single crystals and its Characterisation.
   Physica B 404 (2009) 3886–3889
   Chitharanjan Rai, *K.Sreenivas and S M Dharmaprakash.*

2. Improved ferroelectric and pyroelectric parameters in iminodiacetic acid doped TGS crystal.
   Journal of Crystal Growth , 312 (2010) 273–275
   Chitharanjan Rai*, K.Sreenivas and S M Dharmaprakash*

3. 8 MeV electron irradiation effect on the dielectric and optical properties of iminodiacetic acid doped ferroelectric triglycine sulphate crystals.
   Nuclear Instruments and Methods in Physics Research B 268 (2010) 2510–2514
   Chitharanjan Rai, *Ganesh Sanjeev and S.M. Dharmaprakash.*

4. Iminodiacetic acid doped ferroelectric triglycine sulphate crystal: Crystal growth and characterization.
   Physica B 406 (2011) 1–7
   Chitharanjan Rai, *B. Narayana Moolya and S.M. Dharmaprakash*

5. Crystal Growth, Dielectric, Mechanical, Electrical and Ferroelectric Characterisation of n-Bromo Succinimide doped Triglycine Sulphate Crystals.

   Physica B 406 (2011) 3308 - 3312

   Chitharanjan Rai, *K. Byrappa and S.M.Dharmaprakash*

6. 4-(dimethylamino) benzaldehyde doped Triglycine Sulphate single crystals: Dielectric, Ferroelectric and Conductivity Studies.

   Chitharanjan Rai*, and S M Dharmaprakash (communicated)*

7. Growth and characterization of Succinic acid doped TGS single crystals. *(communicated)*

   Chitharanjan Rai*, and S M Dharmaprakash (communicated)*

LIST OF RESEARCH PAPERS PRESENTED IN NATIONAL AND INTERNATIONAL CONFERENCES / SYMPOSIUMS

1. National Seminar on modern trends in materials science held at University of Calicut, Calicut on 29th and 30th Aug 2005

   "Growth and characterization of 4-(dimethylamino) benzaldehyde Doped Tri Glycine Sulphate single crystal".

2. 50th Annual DAE Solid State Physics Symposium held at BARC, Mumbai from 5th to 9th December 2005.

   "Optical and Electrical Properties of p-Dimethylamino Benzaldehyde doped TGS Single Crystal"

3. 51st Annual DAE Solid State Physics Symposium held at Barkatullah University of Bhopal, Bhopal from 26th to 30th December 2006.

   "Effect of High-Energy Electron Irradiation on Optical Parameters of Succinic Acid Doped Triglycine Sulphate Single Crystals"

4. National Conference on current trends in Material Science CTMS – 07 held at Christian College, Chengannur, Kerala from 25th to 27th march 2007.

   "Growth and characterization of N-bromo succinimide doped Tri-glycine Sulphate single crystal"

5. 52nd Annual DAE Solid State Physics Symposium held at Mysore University, Mysore from 27th to 31st December 2007.

"Dielectric and Hardness studies of n-bromo sccinimide Doped Triglycine Sulphate Single Crystals"

6. The 2nd International Solvothermal & Hydrothermal Association Conference, Beijing, China from 27th to 29th July 2010.

" Iminodiacetic acid doped TGS crystals: Growth and characterization".

7. DAE-BRNS Symposium on Atomic, Molecular and Optical Physics at Karnatak University, Dharwad, during February 22-25, 2011.

"8MeV Electron Radiation Effects on Dielectric and Pyroelectric properties of 4-(dimethylamino) benzaldehyde doped Triglycine Sulphate Crystals.

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